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<p>(54) Title: PREPARATION OF 2,6-NAPHTHALENEDICARBOXYLIC ACID</p> <p>(57) Abstract</p> <p>Disclosed is a process for the manufacture of 2,6-naphthalenedicarboxylic acid (NDA) by the liquid phase oxidation of 2,6-dimethylnaphthalene (DMN) with a molecular oxygen-containing gas in the presence of a catalyst system comprising cobalt, manganese and bromine and a solvent/reaction medium comprising acetic acid containing at least 15 weight percent water. The use of at least 15 weight percent water produces a crude NDA that contains relatively small amounts of residual catalyst metals in comparison to crude NDA produced by similar processes known in the art. In addition, the process results in a lower amount of the acetic acid solvent/reaction medium being oxidized (decomposed) during the oxidation process.</p> <p style="text-align: center;">BEST AVAILABLE COPY</p>		

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PREPARATION OF 2,6-NAPHTHALENEDICARBOXYLIC ACID

REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No.
5 60/060,915 filed October 03, 1997.

FIELD OF THE INVENTION

This invention pertains a process for the liquid phase oxidation of
2,6-dimethylnaphthalene (DMN) with a molecular oxygen-containing gas to
10 produce 2,6-naphthalenedicarboxylic acid (NDA). More specifically, this
invention pertains to an improved process for the preparation of NDA by the
liquid phase oxidation of DMN in the presence of a catalyst system
comprising cobalt, manganese and bromine and a solvent/reaction medium
comprising acetic acid containing at least about 15 weight percent water.
15 The process of the present invention produces crude NDA containing very
low levels of residual catalyst metals and results in less acetic acid being
decomposed.

BACKGROUND OF THE INVENTION

20 NDA is employed as a monomer for the production of several, high
performance polyesters, e.g., liquid crystal polymers and poly(ethylene
2,6-naphthalenedicarboxylate), and polyamides. For example,
poly(ethylene 2,6-naphthalenedicarboxylate) (PEN) exhibits gas barrier
properties which are superior to poly(ethylene terephthalate) (PET) and
25 also can be used for the fabrication of hot-fill plastic containers. NDA
typically is prepared by the liquid-phase, autoxidation of a
dialkylnaphthalene, especially DMN, in the presence of a heavy metal
catalyst system comprising cobalt, manganese and bromine. The crude
oxidation product normally contains too many impurities to be used directly
30 in the synthesis of polymers. Such impurities can affect adversely the

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performance and color of polymers prepared from the impure NDA and can interfere with the polymerization process. These impurities may include the catalyst metals themselves in addition to organic impurities formed during the oxidation. A major impurity formed during the liquid-phase oxidation of DMN is trimellitic acid (TMA). Not only does the formation of TMA represent a yield loss, but TMA may form an insoluble complex with the catalyst metals, thereby causing precipitation of the catalyst metals from the solvent/reaction medium. The precipitation of the catalyst metals leads to deactivation of the homogeneous catalyst system and contamination of the NDA product. Removal of impurities from the crude NDA product is necessary but very difficult. The melting point of NDA is $>300^{\circ}\text{C}$ and it has very low solubility in most organic solvents.

Conversion of NDA to its dimethyl ester (NDC) probably represents the best method for purification. However, the formation of the dimethyl ester alone does not give a sufficiently pure monomer and the NDC must be purified further. U.S. Patent 5,254,719 discloses that NDA may be purified by reaction with methanol in the presence of sulfuric acid. The sulfuric acid solubilizes the catalyst metals and allow their removal with the mother liquor. The resulting dimethyl 2,6-naphthalenedicarboxylate (NDC) is recrystallized and distilled. However, if the catalyst metals are not removed from the NDC purification stream prior to distillation, they can cause fouling and plugging of the distillation column and the heat exchanger (reboiler) utilized as the heat source for the distillation. It also is desirable to recover the catalyst metals due to their expense.

Another method of removing catalyst metals from NDA is described in U.S. Patent 5,183,933. According to the process disclosed in this patent, sufficient water is added to an oxidizer effluent containing NDA to produce a 30 weight percent aqueous solution (30% water/70%acetic acid) which causes the catalyst metals to remain in solution and allow their separation from the solid NDA. However, the mother liquor remaining after

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separation of the solid NDA contained too much water to be recycled directly to the oxidation process described in the '933 patent. Thus, the process of U.S. 5,183,933 requires the removal of some of the water from the mother liquor before it is returned to the oxidizer. In addition, the catalyst metals are recovered for reuse in the oxidation process by precipitation as their oxalic acid complexes following concentration of the mother liquor. A disadvantage of this method is that trimellitic acid (TMA) remains in the mother liquor. According to U.S. 5,189,933, TMA inhibits the oxidation and causes by-product formation when added to the oxidation. Thus, some or all of the TMA should be removed from the mother liquor before it is recycled to the oxidizer.

SUMMARY OF THE INVENTION

We have discovered a means for oxidizing a dimethylnaphthalene (DMN) to produce a crude NDA that contains relatively small amounts of residual catalyst metals in comparison to crude NDA produced by similar processes known in the art. In addition, our novel process results in a lower amount of the acetic acid solvent/reaction medium being oxidized (decomposed) during the oxidation process. The present invention provides a process for the preparation of naphthalenedicarboxylic acid, preferably 2,6-naphthalenedicarboxylic acid (NDA) by the liquid phase oxidation of a dimethylnaphthalene, preferably 2,6-dimethylnaphthalene (DMN) with a molecular oxygen-containing gas in the presence of a catalyst system comprising cobalt, manganese and bromine and a solvent/reaction medium comprising acetic acid and at least 15 weight percent water under oxidation conditions of temperature and pressure.

DETAILED DESCRIPTION OF THE INVENTION

The oxidation process of the present invention wherein a dimethylnaphthalene such as 2,6-dimethylnaphthalene (DMN) is contacted with a

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molecular oxygen-containing gas to obtain a naphthalenedicarboxylic acid such as 2,6-naphthalenedicarboxylic acid (NDA) is carried out in the liquid phase in the presence of a catalyst system comprising cobalt, manganese and bromine and a solvent/reaction medium comprising acetic acid and at least 15 weight percent water at elevated temperature and pressure. The cobalt and manganese components may be provided in any of their known ionic or combined forms that provides cobalt and manganese dissolved in the acetic acid/water, solvent/liquid reaction medium. For example, one or more of cobalt and manganese acetate tetrahydrate, carbonate or bromide may be employed. The bromine component of the catalyst system may be provided by any suitable source of bromine such as, for example, elemental bromine [Br₂], ionic bromide such as HBr, NaBr, KBr, NH₄Br and the like or organic bromine compounds which are known to provide bromide ions at the operating temperature of the process such as, for example, benzyl bromide, mono- and di-bromoacetic acid, bromoacetyl bromide, tetrabromoethane, ethylene dibromide and the like.

The concentrations of the catalyst components in the acetic acid/water solvent/liquid reaction medium normally are about 1000 to 3000 parts per million by weight (ppmw) [Co], about 500 to 3000 ppmw [Mn] and about 500 to 2500 ppmw [Br]. The preferred concentrations of these catalyst components in the acetic acids/water solvent are about 2000 to 3000 ppmw [Co], about 500 to 1200 ppmw [Mn] and about 900 to 2200 ppmw [Br]. The Mn:Co atomic ratio in the reaction zone normally is in the range of about 5:1 to 0.3:1, preferably about 4:1 to 0.5:1 and most preferably about 4:1 to about 2.5:1. Manganese is less expensive than cobalt and therefore it is advantageous to use as much manganese as possible. Generally, high Mn:Co atomic ratios, e.g., ratios greater than about 2.5:1 may give less TMA than Mn:Co atomic ratios of about 1:1. As used herein, "atomic ratio" is the atomic ratio of catalyst components, for example, the ratio of milligram atoms of elemental manganese to milligram

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atoms of elemental cobalt or, in the case of bromine, the milligram atoms of bromine measured as atomic bromine to the total of the milligram atoms of cobalt and milligram atoms of manganese. The atomic ratio of bromine to the total of cobalt and manganese atoms may be in the range of about 0.3:1 to about 0.8:1, preferably about 0.4:1 to 0.7:1. If the atomic ratio of bromine to the total of cobalt and manganese is less than about 0.3:1, a colored product may be produced. If the atomic ratio of bromine to the total of cobalt and manganese exceeds 0.8:1, a large amount of brominated products such as bromonaphthalenedicarboxylic acid may be formed. The individual catalyst components can be introduced into the reaction zone either separately or in one or more combinations in any convenient manner such as, for example, as a solution or solutions in water or a mixture of acetic acid and water.

The process of the present invention is carried out at oxidation-effective conditions of temperature and pressure. The liquid phase oxidation process may be operated at elevated temperatures in the range of about 150 to 220°C, preferably in the range of about 170 to 220 °C and most preferably in the range of about 180 to about 210°C. The process normally is operated at an elevated pressure of at least 3 bar absolute (bara), preferably at a pressure range of about 8 to 23 bara and most preferably at a pressure of about 15 to 21 bara.

The reaction zone may comprise one or more reactors such as tank reactors (preferably stirred), plug flow reactors, compartmented reactors, columnar reactors or a combination of such reactors. For example, the reaction zone can comprise two or three stirred tank reactors arranged in series. Optionally, a plug flow reactor may be used to first mix and pre-heat the reaction mixture before it is fed to the stirred tank reactor or reactors. Another design comprises one or more columnar reactors, optionally equipped with one or more baffles, to which the oxygen-containing gas as fed at or near the bottom by means of a sparging device to create a highly-

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agitated, back-mixed reaction mixture. Normally, the size or capacity of the reactor(s) comprising the reaction zone in combination with the feed rates of DMN and water/acetic acid solvent/liquid reaction medium give a residence time of at least 30 minutes, preferably a residence time of in the
5 range of about 60 to 120 minutes.

The oxidation reaction involved in the invention of the present invention occurs in the liquid phase wherein a catalyst system comprising cobalt, manganese and bromine catalyzes the conversion of the methyl groups of DMN to carboxylic acid groups. The process typically is carried
10 out by feeding to a reaction zone DMN, a gas containing molecular oxygen, the catalyst components and acetic acid which functions as a solvent for the homogeneous (dissolved) catalyst system and a liquid medium in which the oxidation occurs. A liquid reaction product slurry comprising acetic acid and the substantially insoluble NDA is removed from the reaction zone.
15 Water and carbon oxides are by-products of the process. The oxidation process typically is operated in a continuous manner wherein the feed components are supplied continuously to, and product slurry is continuously removed from, the reaction zone.

The source of molecular oxygen employed in the liquid phase
20 process may be air, oxygen enriched air or substantially pure oxygen. Most preferably, for reasons of economy, the source of molecular oxygen is air. The molecular oxygen-containing gas that is introduced into the reaction zone should be fed at a rate such that the exhaust gas mixture exiting the reaction zone contains from about 0.5 to 8 volume percent oxygen.
25 measured on a solvent-free basis, to avoid formation of explosive gas mixtures.

The solvent/liquid reaction medium employed in the process of the present invention is acetic acid containing at least 15 weight percent, preferably 15 to 30 weight percent water (based on the total weight of the
30 acetic acid and water). Although it is technically possible to use other

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normally-liquid materials, e.g., propionic acid, as the solvent/liquid reaction medium, acetic acid is by far the most economical and technically suitable. The concentration of manganese normally should be less than about 1200 ppmw but may be as high as 2300 ppmw when the acetic acid/water mixture comprises 26 weight percent water. Water concentrations greater than 15 weight percent have been found to prevent cobalt and manganese from precipitating from the acetic acid/water solvent/reaction medium and contaminating the crude NDA product. For example, in an oxidation where the water concentration is about 8 weight percent, the crude NDA was found to contain about 1600 ppmw of cobalt. When the same oxidation is carried out in the presence of an acetic acid/water solvent/reaction medium containing 16 weight percent water, the crude NDA contains only about 321 ppmw of Co. When the water concentration is increased to about 26 weight percent, the crude NDA contains only 119 ppm cobalt. Similar results were obtained with respect to manganese.

We have found that if the manganese concentration in the solvent/reaction medium is greater than 1200 ppmw, manganese precipitates with the crude NDA even at water concentration of 15.8 weight percent. Furthermore, the precipitation of manganese at these conditions also causes the co-precipitation of cobalt. Manganese is employed in the oxidation process to improve the efficiency of the cobalt by reducing the amount of acetic acid solvent that is oxidized, i.e., decomposed, during the oxidation process. We have found that if the oxidation is carried out in the presence of high concentrations of water, the amount of manganese that is needed is greatly reduced. This principle is illustrated by the Comparative Example C-1 wherein the concentration of water is about 8 weight percent and the concentration of manganese is 3840 ppmw. In this example, the amount of carbon oxides (CO and CO₂) produced by the oxidation/decomposition of acetic acid was 1.7 mol/hour. By comparison, a

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similar oxidation that contained about 16 weight percent water but only 1225 ppmw of manganese produced only 0.8 mol/hour of carbon oxides.

The weight ratio of acetic acid:DMN fed to the reaction zone may be in the range of about 2:1 to 12:1, preferably in the range of about 3:1 to 6:1.

5 During the operation of the process, the acetic acid solvent/liquid reaction medium must be replenished due to decomposition of acetic acid. We have found that when the solvent/liquid reaction medium comprises about 15 weight percent water, the acetic acid decomposition rate is approximately one-half the decomposition rate when the solvent/liquid reaction medium
10 contains approximately 7 weight percent water.

The oxidation reaction is an exothermic reaction and the heat generated may be dissipated or expelled from the reaction zone in part by the vaporization of acetic acid. Typically, a portion of the vaporized acetic acid is withdrawn from the reaction zone, cooled to condense the vapor,
15 and the condensed liquid is returned to the reaction zone. This vapor typically is a mixture of acetic acid and water. A portion of vaporized acetic acid/water may be subjected to a water removal zone wherein some or substantially all of the water contained in the vapor may be removed prior to returning the condensed vapor to the reaction zone. The water
20 concentration in the reaction zone can thus be adjusted, at least in part, by the use of such a water removal zone. The carbon oxides formed in the process are vented from the reaction zone with the acetic acid/water vapor.

EXAMPLES

25 The oxidation process of our invention is further illustrated by the following examples. The examples were carried out using an apparatus comprising a two-liter, titanium autoclave equipped with an impeller designed for high mass transfer, heating bath, level controller, air inlet, high pressure condenser, heated feed line and double-valved sampling tube.
30 Sample of the crude oxidation product were analyzed for NDA and TMA

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using standard techniques involving the formation of a trimethyl silyl derivative followed by gas chromatography.

EXAMPLES 1-5 AND COMPARATIVE EXAMPLE 1

5 The autoclave was charged with 600 g of acetic acid/water solvent/reaction medium containing varying amounts of cobalt, manganese and bromine provided as cobaltous acetate, manganous acetate, and hydrogen bromide. The solvent/reaction medium comprised varying amounts of acetic acid and water. The autoclave was heated to 205°C and
10 air was sparged through the solvent/reaction medium at a rate 4.2 – 6.0 standard liters per minute. 2,6-DMN and catalyst solution consisting of the mixture described above was pumped into the autoclave via two heated feed lines at the rates shown in Table I. The air flow was adjusted so that the oxygen concentration in the off-gas was maintained at about 5 volume
15 percent. The liquid inventory in the autoclave/reactor was maintained at about 620 g by a level controller. The residence time in the autoclave was 70 to 90 minutes. The oxidation product was removed as a slurry through the double-valved sampling tube at the rate required by the level controller and as shown in Table I. After 3 - 4 residence times, the reaction system
20 reached steady-state operation which was confirmed by the off-gas composition, i.e., the oxygen, carbon dioxide and carbon monoxide content remained substantially constant. The catalyst and DMN feeds were continued for 5 - 8 hours and product samples were collected for analysis every 30 minutes.

25 The average results obtained during steady-state operation for each example are set forth in Table I wherein the values given for water are weight percentages water present in the acetic acid/water solvent/liquid reaction medium, the values given for Catalyst Feed Rate are the g of acetic acid/water solvent/liquid reaction medium containing the cobalt,
30 manganese and bromine catalyst values fed to the autoclave per hour, the

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values given for Co, Mn and Br are the ppmw concentrations of cobalt, manganese and bromine present in the acetic acid/water solvent/reaction medium, the values given for DMN Feed are the mols per hour DMN fed to the autoclave and the values given for NDA are the moles of 2,6-naphthalenedicarboxylic acid produced per hour of operation of the process.

TABLE I

	<u>Example</u>	<u>Water</u>	<u>Catalyst Feed Rate</u>	<u>Co</u>	<u>Mn</u>	<u>Br</u>	<u>DMN Feed Rate</u>	<u>NDA</u>
10	1	15.8	450	2627	1218	1830	0.39	0.37
	2	15.0	490	1244	2300	1718	0.37	0.35
	3	26.4	420	2458	1141	1560	0.34	0.33
	4	15.8	430	2461	1152	1068	0.18	0.16
	5	15.8	410	1246	2304	900	0.34	0.32
15	C-1	7.7	490	2030	3840	1690	0.32	0.30

Table II shows the distribution of catalyst metals (ppmw) in the catalyst feed solution (Feed Solution), in the mother liquor separated from the solid NDA product (Filtrate) and in the solid NDA product (Solids).

TABLE II

	<u>Example</u>	<u>Water</u>	<u>Feed Solution</u>		<u>Filtrate</u>		<u>Solids</u>	
			<u>Co</u>	<u>Mn</u>	<u>Co</u>	<u>Mn</u>	<u>Co</u>	<u>Mn</u>
	1	15.8	2627	1218	2580	824	259	327
25	2	15.0	1244	2300	1150	1410	492	4700
	3	26.4	2458	1141	2140	970	119	141
	4	15.8	2461	1152	2330	1115	447	724
	5	15.8	1246	2304	1039	963	1435	7000
	C-1	7.7	2030	3840	1920	2890	1600	6300

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Table III shows the rates at which carbon oxides (CO_x Rate) (mols per hour) and trimellitic acid (TMA Rate) (weight percent based on weight of NDA produced) as a function of catalyst metal concentration (ppmw) in the feed solution and the water concentration of the acetic acid/water solvent/reaction medium.

TABLE III

10	<u>Example</u>	<u>Water</u>	<u>Feed Solution</u>		<u>CO_x Rate</u>	<u>TMA Rate</u>
			<u>Co</u>	<u>Mn</u>		
	1	15.8	2627	1218	0.09	4.4
	2	15.0	1244	2300	0.8	4.5
	3	26.4	2458	1141	0.6	6.4
	4	15.8	2461	1152	0.9	5.3
15	5	15.8	1246	2304	0.7	6.3
	C-1	7.7	2030	3840	1.7	2.4

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

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CLAIMS

We claim:

1. Process for the manufacture of a naphthalenedicarboxylic acid
5 (NDA) by the liquid phase oxidation of a dimethylnaphthalene (DMN) with a molecular oxygen-containing gas in the presence of a catalyst system comprising cobalt, manganese and bromine and a solvent/reaction medium comprising acetic acid containing at least 15 weight percent water under oxidation conditions of temperature and pressure.
- 10 2. Process according to Claim 1 wherein the oxidation is carried out in the presence of acetic containing 15 to 30 weight percent water having dissolved therein about 1000 to 3000 parts per million by weight (ppmw) [Co], about 500 to 3000 ppmw [Mn] and about 500 to 2500 ppmw [Br].
- 15 3. Process for the manufacture of 2,6-naphthalenedicarboxylic acid by the liquid phase oxidation of 2,6-dimethylnaphthalene with a molecular oxygen-containing gas at a temperature of about 150 to 220°C and a pressure of about 8 to 23 bar absolute in the presence of acetic containing
20 about 15 to 30 weight percent water having dissolved therein about 2000 to 3000 ppmw [Co], about 500 to 1200 ppmw [Mn] and about 900 to 2200 ppmw [Br]
- 25 4. Process according to Claim 3 wherein the oxidation is carried out at a temperature of about 170 to 220°C and a pressure of about 15 to 21 bar absolute.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/19802

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C51/265

According to International Patent Classification (IPC) or to both national classification and IPC

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 183 933 A (HARPER JJ ET AL) 2 February 1993 cited in the application see the whole document, particularly column 5, lines 1-28 ---	1-4
X	US 3 870 754 A (YAMASHITA G ET AL) 11 March 1975 see the whole document, particularly column 4, lines 9-29 --- -/--	1-4

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE WPI Section Ch, Week 9517 Derwent Publications Ltd., London, GB; Class A41, AN 95-128287 XP002091353 & JP 07 053457 A (TEIJIN LTD) , 28 February 1995 see abstract ---	1-4
X	DATABASE WPI Section Ch, Week 9517 Derwent Publications Ltd., London, GB; Class E14, AN 95-126126 XP002091354 & JP 07 048314 A (TEIJIN LTD) , 21 February 1995 see abstract -----	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/19802

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5183933	A	02-02-1993	CA 2098485 A	16-04-1993
			EP 0562105 A	29-09-1993
			JP 6503586 T	21-04-1994
			WO 9308151 A	29-04-1993
US 3870754	A	11-03-1975	NONE	

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